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MEASUREMENT OF EXPOSURE TO EMISSIONS FROM SOUR, SOLUTION GAS FLARES, USING BIOMONITORING METHODS

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MEASUREMENT OF EXPOSURE TO EMISSIONS FROM SOUR, SOLUTION GAS FLARES, USING BIOMONITORING METHODS

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FOREWORD

Polycyclic aromatic hydrocarbons (PAHs) are one of the substances formed during incomplete combustion of organic fuels. In Alberta, oil and gas flares are a source of PAHs, which may lead to the exposure of surrounding vegetation. Two methods can be used to determine exposure; ambient air quality monitoring near the vegetation in the vicinity of a flare or the vegetation itself. This project was designed to investigate the use of biomonitoring methods to measure the exposure of vegetation to the emissions from sour gas flares.

The Air Research Users Group previously supported the review "Evaluation of Polycyclic Aromatic Hydrocarbon (PAH) Accumulation in Plants, The Potential Use of PAH Accumulation as a Marker of Exposure to Air Emissions From Oil and Gas Flares" to help determine if investigations into the use of PAH accumulation in vegetation should be pursued. This study is the first of two follow-up studies that investigate PAH accumulation in vegetation.

Laura Blair
Project Coordinator
Air Research Users Group
Environmental Policy Branch

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SUMMARY

This field study investigates the feasibility of using biomonitoring methods for detection of the exposure of vegetation to emissions of polycyclic aromatic hydrocarbons (PAHs) from sour gas flares. The major objectives were to determine if PAHs could be detected at reasonable concentrations (above the detection limit of the analytical method) and are there detectable PAH concentration gradients with distance and prevailing wind direction around sour solution gas flares.

Based on the study criteria, two test sites (Anadarko Canada, Rocky Mountain House and Husky Oil, Taber) and two control sites (Kananaskis and Vulcan) were selected for collection of vegetative material (pine needles and canola leaves).

Although PAH concentrations in the vegetation were low (many samples were close to the analytical detection limit), concentrations at both test sites were significantly higher than concentrations at the control sites. The data does appear to show a trend of higher concentrations of PAHs at sites closer to the flares; however, the five analytical samples had to be combined to provide sufficient material to exceed detection levels thus analysis to determine if there was a variation in concentration with direction could not be performed. If the method used in this study is to be employed in other studies, larger samples (50 to 100g per sample) should be used in the extraction procedure to increase the concentrations detected. This would increase the confidence levels associated with the test.

1.0 INTRODUCTION

This project derives from a comprehensive literature review by Slaski, Archambault, and Li entitled "Evaluation of Polycyclic Aromatic Hydrocarbon (PAH) Accumulation in Plants: The Potential Use of PAH Accumulation as a Marker of Exposure to Air Emissions from Oil and Gas Flares", published in February 2000. The review article describes the increasingly widespread use of plant materials as passive and active biomonitors of the ubiquitous PAH compounds. A wide variety of different vegetations have been used successfully as quantitative indicators of exposure to both particulate and gas phase PAHs in ambient air.

Many plant species have been used as both active (plants exposed to PAHs in an artificial, sometimes closed environment) and passive monitoring in the natural habitat. The major advantages of plants as passive monitors are their continual exposure over long periods, and the cost of this method compared to conventional physical and chemical active monitoring protocols. Using coniferous plant species for passive monitoring provides an additional advantage as exposure over more than a one-year period can be assessed.

Since the review article by Slaski *et al.* was published in February 2000, a number of important articles have been published in the research literature. These fell into five main categories related to this project:

- Refinement of the use of Relative Abundance Ratios (RARs) of PAHs
- Distribution of PAHs in Soils
- Spiking Efficiencies of PAHs in Soils
- Detailed Characterization of Urban Aerosol Particles (PM-10) including PAHs in Santiago, Chile
- Measurement of PAHs from a variety of Emission Sources

Relative Abundance Ratios have been investigated in considerable detail by Farant and Gariepy (1998), Sanderson and Farant (2000), and Aubin and Farant (2000). It has been accepted that the procedure to estimate both total and individual PAH concentration be based on the concentration of benzo(a)pyrene, B(a)P. In the latter two papers Farant develops the argument that benzo(b)fluoranthene, B(b)F, degrades more slowly than or at the same rate as other particulate PAHs; therefore, is a better marker for the source (an aluminum smelter) than benzo(a)pyrene. In general, this approach, when applied appropriately, provides a viable alternative to all other means of assessing total PAH exposure.

Cousins *et al.* (1999) discuss details of the vertical distribution of both PCBs and PAHs in soils. Both parameters showed a significant positive correlation with organic carbon content and decreased with soil core depth. Details of analytical procedures were provided. Northcott and Jones (2001), in a set of two papers, provide a review of existing methods of spiking hydrophobic organic compounds into soil and suggest an effective standard spiking procedure for recovery experiments. This involved the addition of known quantities of internal standards, or "spiking" at the beginning of an extraction procedure to allow for the estimation of the recovery efficiency of the extraction method. Using their procedure, mean spike recovery and

associated relative standard deviations of PAHs in soils were very good. Two papers related to the characterization of PAHs that are of some significance to this study are those of bin Abas *et al.* (1995) on the composition of smoke aerosols from biomass combustion in Amazonia and that of Didyk *et al.* (2000) on urban aerosol particles in Santiago, Chile. Both papers described the PAH composition of aerosol particles and details of extraction and analytical methodologies. Several PAHs are known mutagens and carcinogens and this has led to an increase in source apportionment of these compounds. Recent among these have been those of Schauer *et al.* into PAHs from gasoline powered motor vehicles (2002), from burning of foliar fuels (2002), and cooking with seed oils (2002). Oanh *et al.* (2002) conducted a survey of PAH emissions during domestic cooking with various fuel sources.

This project investigates the feasibility of employing biomonitoring methods for the detection of exposure of vegetation to the emissions from sour gas flares. The indicator plants used in this study are *Pinus contorta* (lodgepole pine) and *Brassica napa (*canola) since these provide the geographic distribution appropriate to this study in Alberta. Both have been identified as useful indicator species particularly in the study of uptake of PAHs.

The chemical species monitored in this study included a suite of 16 common polynuclear aromatic hydrocarbons (PAHs) including several suspected carcinogenic PAHs

The major research objectives were to determine:

- Can these chemical species be detected at reasonable concentrations and on a routine basis in these two plant tissues?
- Are there detectable concentration gradients of these chemical species surrounding point source emissions from sour gas flares that are both distance and prevailing wind direction dependent?

2.0 EXPERIMENTAL METHODOLOGY

The experimental design incorporated the following features:

- The experiments were conducted at two separate flaring sites and two parallel control sites. Each flaring or control site was divided into three concentric circles and samples collected at a distance from the point source of approximately 500m, 1km, and 5km. Five replicate samples were collected on each radius in a NW, NE, SE, and SW direction from the point source.
- Pine needles were collected in early July. During the July collection needles from years 2 and 3 growth were collected.
- Canola was collected at the end of July. Due to drought conditions in southern Alberta over the past two years, it was only possible to locate a canola test site where samples were collected in the northeast and southeast quadrants.
- Soil samples were collected at each experimental location.
- Analytical samples were prepared from the pine needles using modifications of existing literature methods. Similarly, existing literature extraction methods will be used for the canola and soil samples. (These methods have already been developed in our laboratory as part of this study). These materials are currently in cold storage.
- PAHs were being estimated qualitatively and quantitatively using standard gas chromatography-mass spectrometry-single ion monitoring (GC-MS-SIM) methodologies. These techniques were applied to pine and canola extracts.

2.1 Site Selection

With the cooperation of Jim Spangelo, Kim Eastlick, and particularly Bill Shearer, all from the Alberta Energy Utilities Board, a set of twenty potential study sites were identified. The criteria for selection were:

- within 180 miles of Calgary
- flared over 80,000 m^3 during February 2001

We assessed these potential sites in the context of this project with two additional criteria:

- the vegetation around the sites (canola or lodgepole pine)
- accessibility to the site (drivable roads within approximately 1km of the sampling site)

These criteria reduced the short-list to six sites. These were all visited to establish their suitability.

The final site selections were:

For lodgepole pine – Anadarko Canada, Battery 61074, at 15-17-06W5 located approximately 35 km northeast of Rocky Mountain House north of Highway 12 and east of Highway 761.

For canola – Husky Oil, Battery 50367, at 03-19-008-16W4 located approximately 15 km southwest of Taber west of Highway 36 and north of Highway 513.

Production figures for the whole of 2000 and for February 2001 for these two flares are shown in Tables 1 and 2, below.

Table 1 Production Figures for 2000 in $m^3 \times 10^3$

	Oil produced	Gas produced	Gas flared	Wells
Anadarko	48,548.9	20,573.4	504.7	15
Husky	72,028.7	1,693.7	1,172.1	173

Table 2 Production Figures for February 2001 in $m^3 \times 10^3$

	Oil produced	Gas produced	Gas flared	Wells
Anadarko	4,052.0	2,289.3	137.1	15
Husky	4,452.0	111.8	86.6	173

The control site for lodgepole pine was selected at Sibbald Lake in Kananaskis Country, and the canola control site was in Vulcan at a site used by Alberta Agriculture for Bertha Armyworm monitoring.

2.2 Vegetation Analysis

It was important to characterize each site by the plant composition in order to understand the complex ecosystem interactions that may have a significant influence on the productivity of the site (Beckingham and Archibald, 1996) and to ensure that the test site and control sites were sufficiently similar for comparative purposes.

The two lodgepole pine sites were characterized by three vegetation stratum, understorey stratum, shrub stratum and tree stratum (Table 3). The understorey stratum consists of forbs and herbs that are less than 1m in height. The shrub stratum consists of vegetation between 1 and 3m. The tree stratum consists of trees greater than 3m. The understorey stratum was assessed using 1m by 1m plots at 5m intervals along a randomly placed 30m transect (modified from Alberta

Environmental Protection, 1994). The percent cover of each species was determined. The shrub stratum was assessed along the same 30m transect with 10m on either side of the 30m transect. Within this 20m by 30m plot percent cover of shrubs and small trees between 1m and 3m was sampled (modified from Alberta Environmental Protection, 1994). The tree stratum was sampled along the same 30m transect using the Point Quarter Method (Kerbs, 1989). Six random points were chosen along the transect line and at each point a perpendicular line from the transect defined four quadrants. In each quadrant, the distance to the nearest living tree was measured, the DBH (diameter at breast height) of the tree was recorded and the species was identified. The percent cover of the trees in the same 20m by 30m plot was determined for each tree species.

A vegetation site assessment was completed on September 24, 2001 at the 3km NW Anadarko site. The vegetation site assessment for the control site in Kananaskis was completed on October 9, 2001. The assessment site was located at Sibbald Creek at the 500m NW site. The vegetation site assessment for both Anadarko and Kananaskis revealed similar plant composition and abundance thus indicating the sites could be used for comparative chemical analysis (Table 3).

2.3 Sample Collection

Lodgepole pine needles were collected from trees located at the edge of openings in the forest canopy. This was for three reasons. It has been reported in the literature that exposure rates are higher in these locations due to turbulent plume behaviour at forest margins (see CTDMPLUS Complex Terrain Dispersion Model Plus Algorithms or Unstable Situations www.epa.gov/scram001/#ctdmplus); branches bearing needles on mature lodgepole pine are only found on crowns on in-stand trees. This can be in excess of 25m from the ground and therefore very inaccessible to long pruners. Finally, if this method is to be applied in a routine monitoring program, accessibility is an important issue. Branches bearing second and third year growth were collected with the aid of an extendable pruner (~15m) to provide needle samples of the two growth years of approximately 10g each. Five different trees were sampled at each sampling site. Samples were stored in brown bags on ice during transportation from the field. All needles were removed and aged the following day, placed in screw-cap jars and stored in a freezer at -10°C.

Canola samples were sampled by removing all leaves from the entire plant, placing them in brown paper bags in a cooler, and transporting these back to the laboratory, where they were stored in a freezer at –10°C. The canola experimental design was modified from a full 360° collection around the flare; to a NE/SE 180° design since no field of canola allowing the full experimental design could be located. A total of 30 samples (6 sites x 5 replicates) were collected at both control and test canola sites.

Soil samples were collected at all location by removing loose overburden to expose the organic horizon. The top 5cm was removed to completely fill (i.e. no airspace) a glass collection jar. Jars were retained in a cooler during collection and transportation, and were stored in a freezer prior to extraction. The soil samples will be extracted and analyzed for PAH content in the next phase of this study.

Table 3 Assessment of vegetation of the Anadarko and Kananaskis sites.

Anadarko		Kananaskis	
Tree species:			
Trembling aspen (*Populus tremuloides*)	25%*	Lodgepole pine (*Pinus contorta*)	30%
Lodgepole pine (*Pinus contorta*)	22.5%	Douglas fir (*Pseudotsuga menziesii*)	15%
Paper birch (*Betula papyrifera*)		White spruce (*Picea glauca*)	15%
White spruce (*Picea glauca*)		Trembling aspen (*Populus tremuloides*)	15%
Shrub species:			
Green Alder (*Alnus crispa*)	32.5%	Green Alder (Alnus crispa)	10%
Bracted honeysuckle (*Lonicera involucrata*)	5%	White spruce (*Picea glauca*)	2%
Willow (*Salix spp.*)	5%		
Understorey:			
Aster (*Aster conspicuus*)	2†	Schreber's moss (*Pleurozium schreberi*)	3
Prickly wild rose (*Rosa acicularis*)	2	Bunchberry (*Cornus canadensis*)	2
Bunchberry (*Cornus canadensis*)	2	Wild rye (*Elymus canadensis*)	2
Wild rye (*Elymus canadensis*)	2	Fireweed (*Epilobium augustifolium*)	2
Bracted honeysuckle (*Lonicera involucrata*)	2	(*Linnaea borealis*)	2
Wintergreen (*Pyrola asarifolia*)	2	Sweet coltsfoot (*Petasites palmatus*)	2
Prickly currant (*Ribes lacustre*)	2	Wintergreen (*Pyrola asarifolia*)	2
Green alder (*Alnus crispa*)	1	Prickly wild rose (*Rosa acicularis*)	2
Fireweed (*Epilobium augustifolium*)	1	Cinquefoil (*Potentilla fruticosa*)	1
Cow parsnip (*Heracleum lanatum*)	1	Wild strawberry (*Fragaria virginiana*)	1
Veiny pea (*Lathyrus venosus*)	1	Lichen species	1
Bishop's cap (*Mitella nuda*)	1	Trembling aspen seedlings (*Populus tremuloides*)	1
Sweet coltsfoot (*Petasites palmatus*)	1	Aster (*Aster conspicuus*)	1
Schreber's moss (*Pleurozium schreberi*)	1	High-bush cranberry (*Vibernum edule*)	1
Trembling aspen seedlings (*Populus tremuloides*)	1	Northern bedstraw (*Galium boreale*)	+
Gooseberry (*Ribes oxyacanthoides*)	1	American vetch (*Vicia americana*)	+
Wood's rose (*Rosa woodsii*)	1		
Northern bedstraw (*Galium boreale*)	+		
American vetch (*Vicia americana*)	+		

* Numbers following the tree and shrub species names indicate the percent cover at that site.
† Numbers or + following the understorey species names indicate the Braun-Blanquet scale.

2.3.1 Sampling Sites

The location of the sampling sites is shown on the map in Figure 1.

A total of 120 samples (60 2nd year and 60 3rd year) of approximately 10g each of pine needles were collected at the Anadarko Lodgepole Pine test site as shown below. Both second and third year needles were collected and extracted for PAH content (Figure 2).

Samples were collected in only three of the four quadrants; NW, SW and SE at the Kananaskis site due to the availability of suitable lodgepole pine stands. Care was taken to select age-classes comparable to those used at the Anadarko site, and this restricted the available sample sites to some extent. Again, five replicates of both second and third year growth needles were collected. To date only third year material has been analyzed by GC-MS-SIM (Figure 3).

Great difficulty was encountered in identifying a suitable canola test site. The canola crop in Alberta has been significantly reduced as a result of severe drought conditions in the south and southwest of the province, and the depressed market value of canola. The experimental design was limited to only 180°, but an additional set of samples due east of the flare was included. Samples were collected at l, 2, and 3 km due east, and 2.5 and 3 km NE, and 2.5 and 3 km SE. Five replicates were collected at each site (Figure 4).

The Vulcan Control Canola site was designed to reflect the sampling pattern at the Taber test site. Five replicate samples were collected at 1.5km and 2.5km NE, 1.5km and 2.5km due E, and 1.5km and 2.5km SE of the plot center (Figure 5).

Figure 1 **Overview of location of sampling sites.**

Figure 2 **Lodgepole pine test site (Anadarko). Diagram of sample collection sites.**

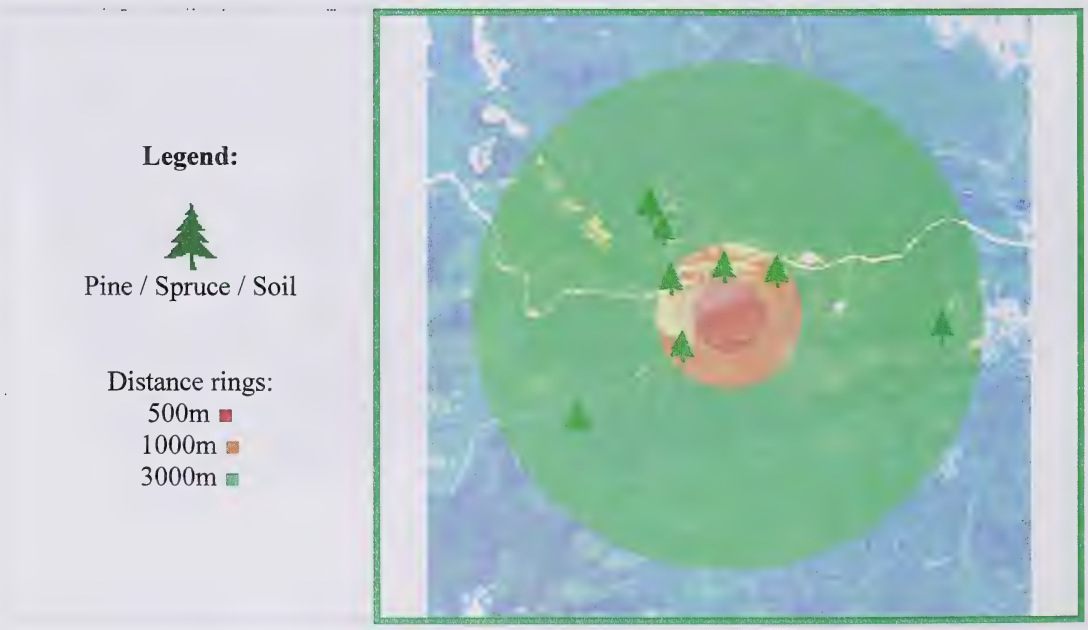


Figure 3 **Lodgepole pine control site (Kananaskis). Diagram of sample collection sites.**

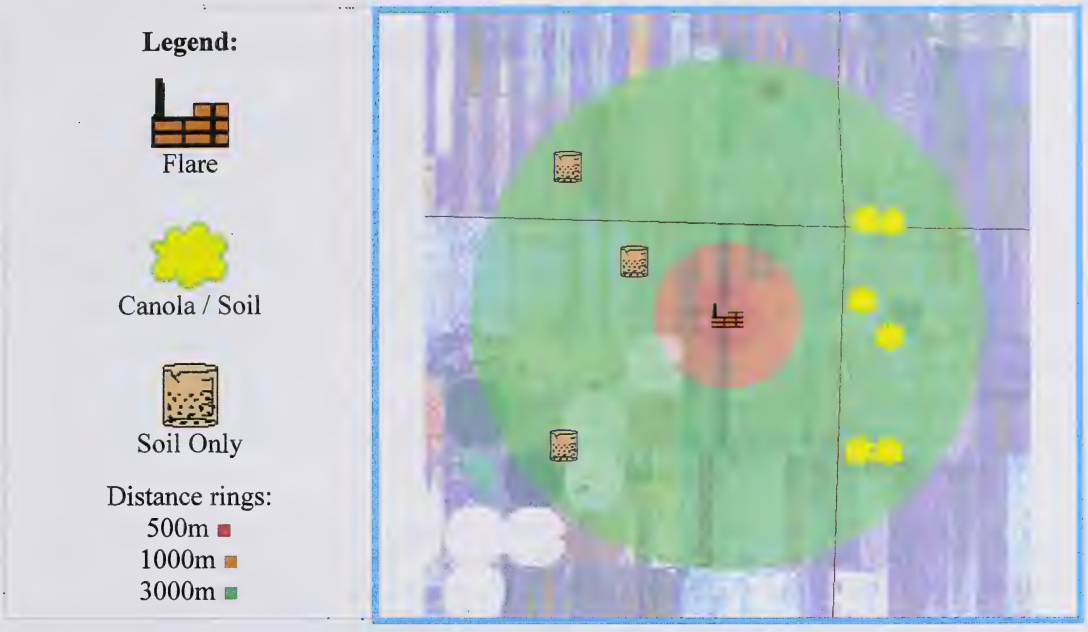


Figure 4 **Canola test site (Taber-Husky). Diagram of sample collection sites.**

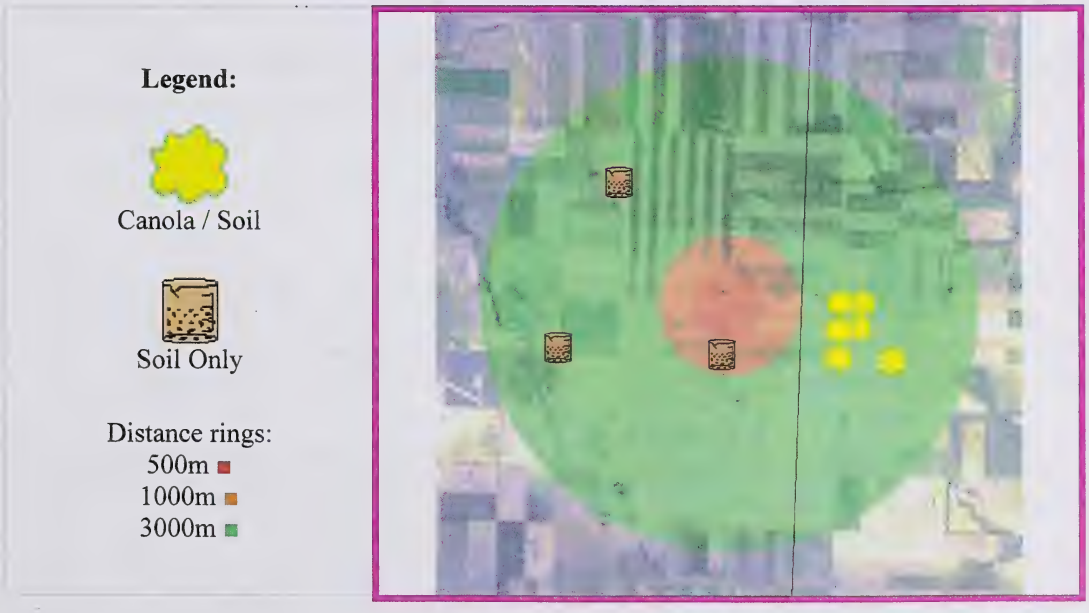


Figure 5 **Canola control site (Vulcan). Diagram of sample collection sites.**

3.0 EXTRACTION OF PAHS FROM NEEDLES AND LEAVES

Naphthalene$_{d-8}$, was used for a series of spike-recovery experiments during the development of the extraction method and subsequently for all PAH extractions. The standard naphthalene$_{d-8}$ solution (40ppm in dichloromethane (DCM)) was diluted tenfold and a spike of 1mL of this solution was added to the needles or leaves. Following this, the needles or leaves were placed in a teflon-lined screw-cap jar and covered with 40mL DCM. This sample was sonicated for 1 hour in a water bath at room temperature to prevent sample heating and possible evaporation of the more volatile PAHs. The solvent was decanted through a hole drilled in a second teflon-lined cap, and filtered by gravity through a Whatman #4 filter paper into a round-bottom flask. An additional 40mL DCM was added to the residual needles or leaves, and the sonication and decantation repeated. The second extract was added to the first and the sample volume reduced to approximately 5mL on a rotary evaporator. Subsequently, the solvent volume was reduced to 0.5mL under a gentle stream of nitrogen.

It was necessary to carry out a clean-up procedure prior to analysis by gas chromatography-mass spectrometry. Initially the method of Guerin (1998) was used. This involved passing the DCM solution through a liquid-solid chromatography column packed with activated silica gel and anhydrous sodium sulphate. Columns were prepared with Pasteur pipettes using DCM as solvent and subsequently as eluant. This procedure was very time consuming, and subsequently commercial silica gel solid phase extraction (SPE) columns were purchased. Later on in the series of analyses, it was found to be necessary to use a far more discriminating solvent system to separate the needle cuticular hydrocarbons, since these had a very strong tendency to adsorb relatively irreversibly to the GC stationary phase. For pine needles it was necessary to strip the cuticular waxes from the sample with 2mL hexane, and elute the remaining PAHs with 2mL toluene in order to separate the waxes from the PAHs. For several of the sites where it was difficult to obtain sample sizes of 10g, needles from trees from the same zone were consolidated.

3.1 GC-MS-SIM Analysis of PAHs

The gas chromatography-mass spectrometry-single ion monitoring (GC-MS-SIM) analyses of the target PAHs were conducted on an HP 5890 gas chromatograph with HP 5970 mass selective detector (MSD). The column used for the gas chromatographic separation was a Hewlett-Packard HP5-MS low-bleed column. Refer to Table 4 for parameter and temperature program.

Each sample was analyzed for the sixteen standard PAHs using the single ion monitoring mode of data collection, in order to maximize the instrument sensitivity. PAHs and their molecular ion with retention times are listed in Table 5.

Table 4 GC-MS-SIM parameters and temperature program

GC/MS parameters		Temperature program	
Injector temperature	275°C	Initial oven temperature	50°C
Detector temperature	300°C	Initial hold time	5.0 min
Oven temperature	300°C	Rate 1	20°C/min
Purge on	1:00 min	Temperature 1	110°C
Equilibrium time	0.50 min	Time for temperature 1	0.0 min
Sample volume	1 µL	Rate 2	7°C/min
		Temperature 2	190°C
		Time for temperature 2	0.0 min
		Rate 3	5°C/min
		Final temperature 3	300°C
		Final hold time 3	5.0
		Total run time	46.4 min

Column type: HP5 MS(30 m X 0.25mm X0.25 µm)

Table 5 List of PAHs Investigated in this Study in order of their GC Retention Times

Name	Molecular Ion (m/e)	Retention Time (mins)
Naphthalene -**NAP**	128	7.41
Acenaphthylene -**ACE**	152	11.13
Acenaphthene -**AL**	154	11.57
Fluorene -**FLU**	166	12.86
Phenanthrene -**PHEN**	178	15.20
Anthracene -**ANTH**	178	15.34
Fluoranthene -**FLT**	202	18.2
Pyrene -**PYR**	202	18.73
Benzo(a)anthracene-**B(a)A**	228	21.78
Chrysene -**CHRY**	228	21.87
Benzo(a)pyrene –**B(a)P**	252	24.52
Benzo(b)fluoranthene – **B(b)F**	252	24.58
Benzo(k)fluoranthene – **B(k)F**	252	25.41
Indeno(1,2,3-c,d)pyrene -**IP**	276	28.66
Dibenz(a,h)anthracene –**D(ah)A**	278	28.66
Benzo(g,h,i)perylene –**B(a)P**	276	29.48

The ions monitored for each candidate PAH were the molecular ion and at least one other qualifying ion, often the M+1 ion peak. Quantitation was carried out by calculating a calibration curve using four standard PAH solutions (0.10, 1.45, 7.36, and 9.98μL/mL). Three internal deuterated standards were used to construct the calibration curve and were subsequently used in all analytical samples. These were:

- Acenaphthene-d10
- Phenanthrene-d10
- Chrysene-d12

4.0 RESULTS

4.1 Treatment and Interpretation of Data

The test site and control site data were tested to determine if they were statistically significantly different. The two pairs of data sets were shown to be different at the 95% confidence level. Detailed statistical analyses concerning the variation of concentration with distance from the flare could not be undertaken since the five separate analytical samples were combined to provide sufficient material to exceed detection levels for the GC-MS detector.

A number of the more volatile PAHs were detected at both test and control sites (Tables 6 and 7). Those found at control sites included Acenapthene, Naphthalene, and Phenanthrene. All of these PAHs have been found in the tailpipe emissions of gasoline-powered motor vehicles at relatively high concentrations (Schauer *et al.*, 2002). Both test sites and control sites had data collection points within 1km of a highway; therefore, should be similarly influenced by PAHs in vehicle exhaust.

The Anadarko lodgepole pine test site revealed samples that contained Acenaphthene, Acenaphthylene , Anthracene, Naphthalene, Fluorene, Fluoranthene, Pyrene and Benzo(a)anthracene. The Anadarko site is relatively sweet gas flare operation and all these PAHs were detected by Strosher (1996) in sweet solution gas flares.

Acenaphthene, Naphthalene, Fluorene, Phenanthrene, Pyrene, and Chrysene were all detected in canola samples at the sour gas flare site at Taber. All these compounds were detected by Strosher (1996) in sour gas flares where incomplete combustion had taken place.

In spite of the low levels of PAHs detected the canola and pine needle data do appear to show a trend of higher concentrations of these compounds at sites closer to the flares (Figures 6 and 7).

Table 6 **Anadarko test site (a) and Kananaskis control site (b) for lodgepole pine. Mass (ng g^{-1} needle wt) for 3rd year needles of 16 selected PAHs in four quadrants at selected distances from the flare or from the plot centre**

	ACE	AL	ANT	NAP	FLU	PHEN	FLT	PYR	B(a)A	CHRY	B(a)P	B(b)F	B(k)F	IP	D(ah)A	BPY
(a)																
NW 0.5	-*	-	0.3	0.1	0.01	-	0.1	0.4	-	-	-	-	-	-	-	-
NW 1.0	0.01	0.1	1.0	-	0.1	-	0.1	-	-	-	-	-	-	-	-	-
NW 5.0	-	0.12	0.2	-	-	-	-	0.1	0.2	-	-	-	-	-	-	-
NE 0.5	-	0.1	0.2	0.5	-	-	-	-	-	-	-	-	-	-	-	-
NE 1.0	-	-	-	0.4	-	-	-	0.5	-	-	-	-	-	-	-	-
NE 5.0	-	0.2	-	0.1	-	-	-	-	0.15	-	-	-	-	-	-	-
SE 0.5	-	-	0.1	-	0.2	-	-	-	-	0.2	-	-	-	-	-	-
SE 1.0	-	-	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-
SE 5.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SW 0.5	0.1	0.1	-	0.37	-	-	-	0.5	-	-	-	-	-	-	-	-
SW 1.0	-	-	-	0.21	-	-	-	1.96	-	-	-	-	-	-	-	-
SW 5.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
(b)																
NW 0.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NW 1.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SW 0.5	0.1	-	-	0.1	-	0.1	-	-	-	-	-	-	-	-	-	-
SW 1.0	0.1	-	-	0.1	-	0.2	-	-	-	-	-	-	-	-	-	-
SW 3.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SE 0.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SE 1.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SE 3.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

* - A dash indicates PAH not detected

Table 7 **Taber test site (a) and Vulcan control site (b) for canola. Mass (ng g^{-1} leaf wt) of 16 selected PAHs in two quadrants at selected distances from flare or from plot centre**

	ACE	AL	ANT	NAP	FLU	PHEN	FLT	PYR	B(a)A	CHRY	B(a)P	B(b)F	B(k)F	IP	D(ah)A	BPY
(a)																
NE 2.5	0.8	-*	-	-	0.2	-	-	-	-	-	-	-	-	-	-	-
NE 3.0	-	-	-	-	-	1.0	-	-	-	-	-	-	-	-	-	-
E 1.0	1.3	-	-	0.3	-	0.8	-	2.0	0.6	0.3	-	-	-	-	-	-
E 2.0	0.9	-	-	0.2	-	0.3	-	0.8	0.2	-	-	-	-	-	-	-
E 3.0	-	-	-	0.2	-	0.2	-	-	-	-	-	-	-	-	-	-
SE 2.5	0.2	-	-	-	-	0.3	-	0.4	0.4	-	-	-	-	-	-	-
SE 3.0	-	-	-	-	-	0.1	-	0.3	0.1	-	-	-	-	-	-	-
(b)																
NE 1.5	-	-	-	0.1	-	-	-	-	-	-	-	-	-	-	-	-
NE 2.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E 1.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E 2.0	-	-	-	0.1	-	-	-	-	-	-	-	-	-	-	-	-
SE 1.5	-	-	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-
SE 2.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

* – A dash indicates PAH not detected

Figure 6 **Mass of PAH per leaf weight of canola (ng PAH/g leaf) with direction and distance (km) from Taber test site flare**

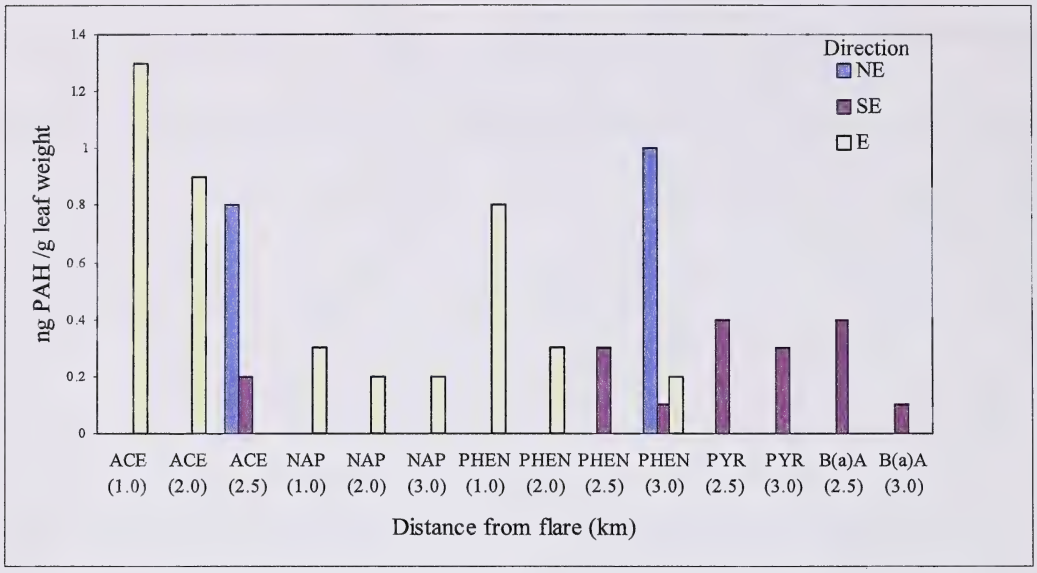
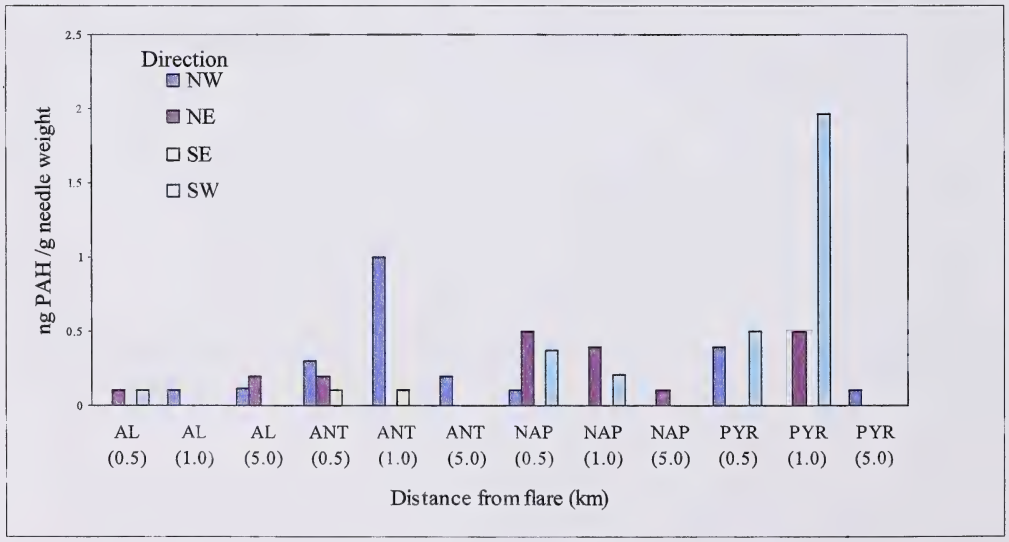


Figure 7 **Mass of PAH per needle weight of pine (ng PAH/g needle) with direction and distance (km) from Anadarko test site flare**



5.0 CONCLUSIONS

These preliminary experiments clearly demonstrate the feasibility of using PAHs as a biomonitoring mechanism for emissions from sweet and sour solution gas flares. Several PAHs are detectable above levels expected from motor vehicular traffic in the area. The 1.0km SW and NW sites showed total PAH concentrations of 2.17 and 1.31ng/g respectively. Previously reported total PAH concentrations in remote rural areas in Europe in *Pinus spp.* are as low as 0.3ng/g (Lehndorff and Schwark, 2004). Therefore the quantities detected in this study indicate elevated PAH concentrations. Concentrations at the Anardarko site were considerably higher than at the Kananaskis control site (highest total PAH concentration – 0.4ng/g), even though the control trees were subject to exposure from infrequent vehicular traffic. At the other end of the concentration scale, pine needles at several urban sites in the UK have been shown to accumulate as much as 3000ng/g total PAHs (Tremolada *et al.*, 1996) and Kale leaves up to 500ng/g total PAHs in Wittlich, Germany (Franzaring *et al.*, 1992)

The levels detected are of the same order of magnitude as those reported in the literature from a variety of emission sources and using several different plant species as the biomonitoring detector (Lodovici *et al.*, 1994 and 1998; Ignesti *et al.*, 1992; Nakajima *et al.*, 1994 and 1995; Tremolada *et al.*, 1996; Wagrowski and Hites, 1997; Yang *et al.*, 1991; Jones *et al.*, 1992; Meharg *et al.*, 1998; Horstman and McLachlan, 1998; Franzaring *et al.*, 1992; Wegener *et al.*, 1992; Thomas *et al.*, 1984; Thomas and Schunke, 1984),

The extraction and analytical procedure for the analysis of PAHs in plant material is extremely time-consuming. Each sample takes 3-4 hours to extract and a further 45 minutes to analyse. The original mandate of this project indicated that, if necessary, new analytical procedures should be developed where appropriate. The methods used are the most widely accepted ones. Hawthorne *et al.* (2000) has reported a significantly shorter (approximately 45 minute) method. This involves the subcritical water and solid phase microextraction of PAHs from a variety of matrixes. Dr. Hawthorne has indicated that he will be more than willing to give detailed advice if we wish to pursue this approach in the future. I recommend that this approach be tested in the future; for a relatively modest investment of time it will be possible to determine if this approach holds any promise for our samples. If these trials are not successful, it is recommended that in future samples of 50 or 100g be used in the extraction procedures. The levels of PAH detected are close to the instrument detection levels, and higher concentrations would increase the confidence levels associated with the determinations

Last year the Canola crop in southern Alberta was compromised due to drought. It is recommended that we repeat these trials this year under far more favourable weather conditions.

To date, only the third year lodgepole pine needles have been analysed. Second year needles were also collected, as well as white spruce needles in the two age classes. These samples have been stored in a freezer since their collection and are still viable samples. It is recommended that these samples be analysed. White spruce may prove to be a better experimental species for two reasons. In southern Alberta towards the edge of the foothills region, white spruce (*Picea glauca)* is more widely distributed. In certain locations difficulty in locating sufficient pine

samples was experienced. In stand lodgepole pine bears very few branches except in the crown region. The crown is often more that 35 feet above the ground, and is therefore extremely difficult to sample. On the other hand, white spruce is more conducive to sampling.

6.0 REFERENCES

The list of references includes all articles directly cited in the text, plus those used as bibliographic background to the entire study.

Addison PA, Puckjett KJ (1980) Deposition of Atmospheric Pollutants as Measured by Lichen Element Content in the Athabasca Oil Sands Area. Canadian Journal of Botany 58: 2323-2334.

Alberta Environmental Protection (1994) Ecological Land Survey Site Description Manual. Alberta Environmental Protection. Resource Information Branch, Finance, Land Information and Programs Support Services, Edmonton, Alberta.

Aprill W, Sims RC (1990) Evaluation of the Use of Prairie Grasses for Stimulating Polycyclic Aromatic Hydrocarbon Treatment in Soil. Chemosphere 20 (1-2): 253-265.

Aubin S, Farant JP (2000) Benzo(b)fluoranthene, a Potential Alternative to Benzo(a)pyrene as an Indicator of Exposure to Airborne PAHs in the Vicinity of Soderberg Aluminum Smelters. Journal of Air and Waste Management Association 50: 2093-2101.

Bacchi E, Calamari D, Gaggi C, Vighi M (1990) Bioconcentrations of Organic Chemical Vapors in Plants Leaves: Experimental Measurements and Correlation. Environmental Science and Technology 24 (6): 885-889.

Bacci E, Cerejeira MJ, Gaggi C, Chemello G, Calamari D, Vighi M (1990) Bioconcentration of Organic Chemical Vapours in Plant Leaves: the Azalea Model. Chemosphere 21 (4-5): 525-535.

Banks MK, Lee E, Schwab AP (1999) Evaluation of Dissipation Mechanisms for Benzo(a) pyrene in the Rhizosphere of Tall Fescue. Journal of Environmental Quality 28: 294-298.

Beckingham JD, Archibald JH (1996) Field Guide to Ecosites of Northern Alberta. UBC Press, Vancouver, B.C.

bin Abas MRB, Simoneit BRT, Elias V, Cabral JA, Cardoso JN (1995) Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in *Amazonia.* Chemosphere 30 (5) 995-1015.

Bohme F, Welsch-Pausch K, McLachlan MS (1999) Uptake of Airborne Semivolatile Organic Compounds in Agricultural Plants: Field Measurements of Interspecies Variability. Environmental Science and Technology 33 (11): 1805-1813.

Calamari D, Bacci E, Focardi S, Morosini M, Vighi M (1991) Role of Plant Biomass in the Global Environmental Partitioning of Chlorinated Hydrocarbons. Environmental Science and Technology 25 (8): 1489-1495.

Carlberg GE, Ofstad EB, Drangsholt H (1983) Atmospheric Deposition of Organic Micropollutants in Norway Studies by Means of Moss and Lichen Analysis. Chemosphere 12 (3): 341-356.

Cousins T, Gevao B, Jones KC (1999) Measuring and Modelling the Vertical Distribution of Semi-volatile Organic Compounds in Soils. I: PCB and PAH Soil Core Data. Chemosphere 39 (14): 2507-2518.

Didyk BM, Simoneit BRT, Pezoa LA, Riveros ML, Flores AA (2000) Urban Aerosol Particles of Santiago, Chile: Organic Content and Molecular Characterization. Atmospheric Environment 34 (8): 1167-1179.

Farant JF, Griepy M (1998) Relationship Between Benzo(a)pyrene and Individual Polycyclic Aromatic Hydrocarbons in a Soderberg Primary Aluminum Smelter. Journal of the American Industrial Hygiene Association 58 (11): 758-765.

Franzaring J, Bierl R, Ruthsatz B (1992) Active Biological Monitoring of Polycyclic Aromatic Hydrocarbons Using Kale (*Brassica oleracea*) as a Monitoring Species. Chemosphere 25 (6): 827-834.

Gardner B, Hewitt CN, Jones KC (1995) PAHs in Air Adjacent to Two Inland Water Bodies. Environmental Science and Technology 29 (9): 2405-2413.

Grimmer G, Jacob J (1987) Recommended Method for the Gas Chromatographic Profile Analysis of Polycyclic Aromatic Hydrocarbons in Smoked Food. Pure and Applied Chemistry 59 (12): 1729-1734.

Gustafason KE, Dickhut RM (1997) Particle/Gas Concentrations and Distributions of PAHs in the Atmosphere of Southern Chesapeake Bay. Environmental Science and Technology 31 (1): 140-147.

Hawthorne SB, Grabanski CB, Martin E, Miller DJ (2000) Comparison of Soxhlet Extraction, Pressurized Liquid Extraction, Supercritical Fluid Extraction, and Subcritical Water Extraction for Environmental Solids. Recovery, Selectivity, and Effects on Sample Matrix. Journal of Chromatography A 892 (1-2): 421-433.

Hays MD, Geron CD, Linna KJ, Smith ND, Schauer JJ (2002) Speciation of Gas-Phase and Fine Particle Emissions from Burning of Foliar Fuels. Environmental Science and Technology 36 (11): 2281-2295.

Horstmann M, McLachlan MS (1998) Atmospheric Deposition of Semivolatile Organic Compounds in Two Forest Canopies. Atmospheric Environment 32 (10): 1799-1809.

Howsam M, Jones KC, Ineson P (2001) Dynamics of PAH Deposition, Cycling and Storage in a Mixed-Deciduous (*Quercus-Raxinus*) Woodland Ecosystem. Environmental Pollution 13: 163-176.

Ignesti G, Lodovici M, Dolara P, Lucia P, Grechi D (1992) Polycyclic Aromatic Hydrocarbons in Olive Fruits as a Measure of Air Pollution in the Valley of Florence (Italy). Bulletin of Environmental Contamination and Toxicology 48: 809-814.

Jones KC, Duarte-Davidson R (1997) Transfer of Airborne PCDD/Fs to Bulk Deposition Collectors and Herbage. Environmental Science and Technology 31 (10): 2937-2943.

Jones KC, Grimmer G, Jacob J, Johnston AE (1989) Changes in the Polynuclear Aromatic Hydrocarbon Content of Wheat Grain and Pasture Grassland Over the Last Century from One Site in the U.K. The Science of the Total Environment 78: 117-130.

Jones KC, Sanders SR, Wild SR, Burnett V, Johnston AE (1989) Evidence for a Decline of PCBs and PAHs in Rural Vegetation and Air in the United Kingdom. Nature 356: 137-139.

Jones KC, Stratford JA, Waterhouse KS, Vogt NB (1989) Organic Contaminants in Welsh Soils: Polynuclear Aromatic Hydrocarbons. Environmental Science and Technology 23 (5): 540-550.

Jones KC, Wild SR, Johnston AE (1992) The Polynuclear Aromatic Hydrocarbon PAH Content of Herbage from a Long-term Grassland Experiment. Atmospheric Environment 26 (7): 1299-1307.

Kerbs CJ (1989) Ecological Methods. Harper Collins.

Komp P, McLachlan MS (1997) Interspecies Variability of the Plant/Air Partitioning of Polychlorinated Biphenyls. Environmental Science and Technology 31 (10): 2944-2948.

Kylin H, Grimvall E, Ostman C (1994) Environmental Monitoring and Polychlorinated Biphenyls Using Pine Needles as Passive Samplers. Environmental Science and Technology 28 (7): 1320-1324.

Leahey DM, (1996) Estimated Ground Level Concentrations of Products of Incomplete Combustion(PIC) Associated with Flaring Activities at Two Sites in Alberta. In "Investigations of Flare Gas Emissions in Alberta). ARC Report, Calgary, AB., 30pp.

Lehndorff E, Schwark L (2004) Biomonitoring of air quality in the Cologne Conurbation using pine needles as a passive sampler – Part II: polycyclic aromatic hydrocarbons (PAH). Atmospheric Environment 38: 3793-3808.

Lodovici M, Akpan V, Casalini C, Zappa C, Dolara P (1998) Polycyclic Aromatic Hydrocarbons in *Laurus nobilis* Leaves as a Measure of Air Pollutants in Urban and Rural Sites of Tuscany. Chemosphere 36 (8): 1703-1712.

Lodovici M, Dolara P, Taiti S, Del Carmine P, Bernardi L, Agati L, Ciappellano S (1994) Polynuclear Aromatic Hydrocarbons in the Leaves of the Evergreen Tree *Laurus nobilis*. The Science of the Total Environment 153: 61-68.

Meharg AA, Wright J, Dyke H, Osborne D (1998) Polycyclic Aromatic Hydrocarbons (PAH) Dispersion and Deposition to Vegetation and Soil Following a Large-Scale Chemical Fire. Environmental Pollution 99: 29-36.

Meredith ML, Hites RA (1987) Polychlorinated Biphenyl Accumulation in Tree Bark and Wood Growth Rings. Environmental Science and Technology 21 (7): 709-712.

Nakajima D, Teshima T, Ochiai M, Tabata M, Suzuki J, Suzuki S (1994) Determination of 1-Nitropyrene Retained in Leaves of Roadside Trees. Bulletin of Environmental Contamination and Toxicology 53 (6): 888-894.

Nakajima D, Yoshida Y, Suzuki J, Suzuki S (1995) Seasonal Changes in the Concentration of Polycyclic Aromatic Hydrocarbons in Azalea Leaves and the Relationship to Atmospheric Concentration. Chemosphere 30 (3): 409-418.

Northcott GL, Jones KC (2001) Partitioning, Extractability, and Formation of Nonextracted PAH Residues in Soil. 2. Effects on Compound Dissolution Behaviour. Environmental Science and Technology 35 (6): 1111-1117.

Oanh NTK, Nghiem LH, Phyu YL (2002) Emission of Polycyclic Aromatic Hydrocarbons, Toxicity, and Mutagenicity from Domestic Cooking Using Sawdust Briquettes, Wood, and Kerosene. Environmental Science and Technology 36 (5): 833-839.

Pathirana S, Connell DW, Vowles PD (1994) Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in an Urban Roadway System. Ecotoxicology and Environmental Safety 28: 256-269.

Reilley KA, Banks MK, Schwab AP (1996) Organic Chemicals in the Environment: Dissipation of Polycyclic Aromatic Hydrocarbons in the Rhizosphere. Journal of Environmental Quality 25: 212-219.

Reischl A, Reissinger M, Hutzinger O (1987) Occurrence and Distribution of Atmospheric Organic Micropollutants in Conifer Needles. Chemosphere 16 (10-12): 2647-2652.

Reischl A, Reissinger M, Thoma H, Hutzinger O 1989. Accumulation of Organic Air Constituents by Plant Surfaces: Part IV a Sampling System for Atmospheric Polychlordibenzo-p-dioxin (PCDD) and Polychlorodibenzo-p-furan (PCDF). Chemosphere: 18 (1-6): 561-568.

Safe S, Brown KW, Donnelly KC, Anderson CS, Marklewicz KV (1992) Polychlorinated Dibenzo-p-dioxins and Dibenzofurans Association with Wood-Preserving Chemical Sites: Biomonitoring with Pine Needles. Environmental Science and Technology 26 (2): 394-396.

Sanderson EG, Farant JP (2000) Use of Benzo(a)pyrene Relative Abundance Ratios to Assess Exposure to Polycyclic Aromatic Hydrocarbons in the Ambient Atmosphere in the Vicinity of a Soderberg Aluminum Smelter. Journal of Air and Waste Management Association 50: 2085-2092.

Schwab AP, Al-Assi AA, Banks MK (1998) Adsorption of Naphthalene onto Plant Roots. Journal of Environmental Quality 27: 220-224.

Schauer JJ, Fraser MP, Cass GR, Simoneit BRT (2002) Source Reconciliation of Atmospheric Gas-phase and Particle-phase Pollutants During a Severe Photochemical Smog Episode. Environmental Science and Technology 36 (17): 3806-3814.

Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT (2002) Measurement of Emissions from Air Pollution Sources. 4. C_1-C_{27} Organic Compounds from Cooking with Seed Oils. Environmental Science and Technology 36 (4): 567-575.

Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT (2002) Measurement of Emissions from Air Pollution Sources. 5. C_1-C_{32} Organic Compounds from Gasoline-Powered Motor Vehicles. Environmental Science and Technology 36 (6): 1169-1180.

Simonich SL, Hites R (1994a) Vegetation-Atmosphere Partitioning of Polycyclic Aromatic Hydrocarbons. Environmental Science and Technology 28 (5): 939-943.

Simonich SL, Hites R (1994b) Importance of Vegetation in Removing Polycyclic Aromatic Hydrocarbons from the Atmosphere. Nature 370: 49-51.

Slaski, Archambault, Li (2000) Evaluation of Polycyclic Aromatic Hydrocarbon (PAH) Accumulation in Plants: The Potential Use of PAH Accumulation as a Marker of Exposure to Air Emissions from Oil and Gas Flares" Alberta Environment.

Smith JN, Levy EM (1990) Geochronology for Polycyclic Aromatic Hydrocarbons Contamination in Sediments of the Saguenay Fjord. Environmental Science and Technology 24 (6): 874-879.

Strachan WMJ, Glooschenko WA (1988) Moss Bags as Monitors of Organic Contamination in the Atmosphere. Environmental Contamination and Toxicology 40: 447-450.

Strosher M, (1996) Investigations of Flare Gas Emissions in Alberta. ARC Report, Calgary, AB., 111pp.

Thomas W (1984) Statistical Models for the Accumulation of PAH, Chlorinated Hydrocarbons and Trace Metals in Epiphytic *Hypnum cupressiforme*. Water, Air, and Soil Pollution 22: 351-371.

Thomas W, Ruhling A, Simon H (1984) Accumulation of Airborne Pollutants (PAH, Chlorinated Hydrocarbons, Heavy Metals in Various Plant Species and Humus. Environmental Pollution (Series A) 36: 295-310.

Thomas W, Schunke E (1984) Polyaromatic Hydrocarbons, Chlorinated Hydrocarbons, and Trace Metals in Moss Samples from Iceland. Linbergia 10 (1): 27-32.

Tremolada P, Burnett V, Calamari D, Jones KC (1996) Spatial Distribution of PAHs in the U.K. Atmosphere Using Pine Needles. Environmental Science and Technology 30 (12): 3570-3577.

U.S. Environmental Protection Agengy Technology Transfer Network. Support Center for Regulatory Air Models. www.epa.gov/scram001/#ctdmplus.

Wagrowski DM, Hites RA (1997) Polycyclic Aromatic Hydrocarbons Accumulation in Urban, Suburban, and Rural Vegetation. Environmental Science and Technology 31 (1): 279-282.

Wegener JWM, van Schaik MJM, Aiking H (1992) Active Biomonitoring of Polycyclic Aromatic Hydrocarbons by Means of Mosses. Environmental Pollution 76: 15-18.

Welsch-Pausch K, McLaghlan, MS, Umlauf G (1995) Determination of the Principle Pathways of Polychlorinated Dibenzo-p-dioxin and Dibenzofurans to *Loium multiflorum* (Welsh Ray Grass). Environmental Science and Technology 29 (4): 1090-1098.

Wild SR, Jones KC 1991. Studies on the Polynuclear Aromatic Hydrocarbon Content of Carrots (*Daucus carota)*. Chemosphere 23: 243-251.

Yang SYN, Connell DW, Hawker DW, Kayal SI (1991) Polycyclic Aromatic Hydrocarbons in Air, Soil, and Vegetation in the Vicinity of an Urban Roadway. The Science of the Total Environment 102: 229-240.

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